

Bioavailability Of Heavy Metals In Epipelagic Sediments And Tissues Of African Catfish (Clarias Gariepinus) Of The Kolo Creek, Bayelsa State, Nigeria

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Abstract—The total heavy metal concentrations and digestion technique was employed to investigate five environmentally toxic heavy metals in two matrices (sediments and fish tissues) of the Kolo Creek, Niger Delta Region, Nigeria, in order to evaluate their potential bioavailability and contamination risk. The concentrations of heavy metals in each matrix were determined using a GBC Avanta PM. Ver 2.02 AAS. The mean concentrations (mg/kg) in sediments were: 2.22 ± 2.48 (Cd), 7.39 ± 4.75 (Cu), 15499.02 ± 1454 (Fe), 6.00 ± 4.47 (Pb) and 35.19 ± 22.15 (Zn), while the mean levels (mg/kg) of heavy metals in biota were: (0.37 ± 0.15) Cd, (3.21 ± 0.15) Cu, (110.33 ± 46.99) Fe, (1.60 ± 1.55) Pb and (26.86 ± 8.24) Zn respectively. The heavy metal concentrations in sediments and biota were compared with World Health Organization (WHO), US Environmental Protection Agency (USEPA) and, Sediment Quality Guidelines (SQG) values to infer anthropogenic input from natural input and no significant toxicity was observed. Furthermore, PCM analysis reveals a positive correlation between the metal ions; this could indicate a common source for all the metals, however, very few of the metals are significantly correlated with each other. This behavior could indicate non-point source.

Keywords—Heavy metal, Biota, Matrices, Kolo Creek, Bioavailability, Contamination risk

1. INTRODUCTION

The search for crude oil, natural gas and other natural resources in the Niger Delta has brought about urbanization and industrialization in the region. Consequently, this activity has led to stress in rivers, other water bodies and the aquatic ecosystem. Kolo

Creek ecosystem is known for its biodiversity and aesthetic value but continuous release of pollutants into the river may diminish its worth. Due to the morphological, climatological and ecological characteristics of the Niger Delta region of Nigeria, Kolo creek is a suitable habitat for a variety of aquatic animals, particularly fish.

The presence of heavy metals in the environment is of great ecological significance due to their toxicity at certain concentrations, transference through food chains and non-biodegradability which is responsible for their accumulation in the biosphere. The behaviour and biological impact of heavy metal pollutants in aquatic systems is influenced by factors, such as adsorption, desorption, sedimentation, suspension, filtration, complexation, precipitation, solubilization, biological uptake and excretion [23]; [18]. The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution [8], [14]. The concentration of metals in sediments is often treated as an indicator of anthropogenic contamination of rivers and lakes. Sediments are integral and inseparable parts of the aquatic environments because they help to determine the overall assessment of heavy metals in water vis-avis aquatic life and its survivability [1],[21]. Heavy metal concentrations in aquatic ecosystems are usually studied by investigating their concentrations in water, sediments and associated biota [6], [10]. Generally, which exist in low levels in water and attain considerable accumulation in sediment and biota [17]. There is a great variety of chemical methods to extract heavy metals from soils and sediments. Heavy metals are in dynamic equilibrium with the overlying water column and have pathways that are primarily associated with sediment substrates in aquatic ecosystems [7], [3]. In assessing the pollution status of aquatic ecosystem,

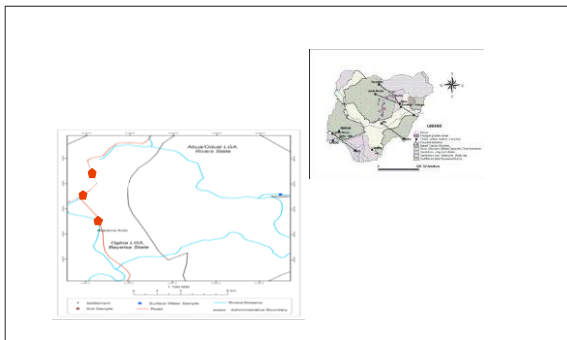
the quality of sediment is therefore essential, because sediments constitute the most important sink of heavy metals and other pollutants [2].

The use of sediment as bio-indicator in pollution study in this area has not also received much attention. The aim of the present study is to evaluate the level of bioavailability and contamination risk of five essential heavy metals (cadmium, copper, iron, lead and zinc), iron appearing with increased accumulation in the sediments and the fish. However, *clarias gariepinus* is of great conservation and economic importance in the Niger Delta Region, and Nigeria at large. The results of this study could provide additional data on the Kolo Creek system. The data and finding of this research can also be useful as a baseline for the management and sustainable development of the study area.

2. MATERIALS AND METHODS

2.1 Description of study area

The Kolo Creek is a natural river geographically located in Bayelsa state, Niger Delta region, Nigeria (Fig. 1). The river lies between the coordinates of latitude $4^{\circ} 53' 15.855''$ North and longitude $6^{\circ} 22' 25.640''$ East. The river is surrounded by a number of water bodies that drain into it: natural and artificial lakes, ponds, burrow pits and tributaries. It is a freshwater non-tidal river that empties into the Nun River.



Source: [15]

Figure 1. Map showing sampling stations

2.2 Sampling and Analysis

2.2.1 Sediment sample

In this study, sediment samples were collected from three stations: upstream, middle reach and downstream along the Kolo Creek system. Sediments were sampled using a bottom grab sampler (Hydro-Bios) and then immediately transferred into plastic bags and refrigerated. In order to get a representative sample for each station, several sub-samples were collected and mixed together. At the laboratory, the samples were air dried, ground and sieved through a 2 mm mesh to remove dirt and other debris, then stored in closed plastic containers. 1g of sediment oven dried at $105^{\circ}\text{C} + 5\text{ml HF}$ in a Teflon beaker digested in water bath at 1000°C for 1 hour. Another 5ml HF + 5ml HNO_3 then heated for 1.5 hours. Then, cooling at room

temperature + 20ml of to prevent residual HF which would otherwise attack glasswares. The digested sediments was filtered into 100ml volumetric flask and made up to mark

2.2.2 Test Animal Description and Sample digestion

The test animals used for this study are African catfish (*Clarias gariepinus*). They are black on the dorsal surface with dark green or olive colour and white on the ventral surface. The head is dorso-ventrally flattened, with skin usually smooth in the young and coarsely granulated in adult. *Clarias gariepinus* also called African catfish belongs to the Phylum; Chordata, Class; Osteichthyes, Order; Siluriformes, Family; Clariidae (air breathing fishes [5]).

Each fresh fish was properly cleaned by rinsing with distilled water to remove external adherent. It was then drained and frozen at -10°C . To study the elemental body burden, the samples were thawed out for several hours and separated into gills and muscles. The fish parts were dried at 80°C to constant weight. The dried pooled fish samples were homogenized thoroughly in an electric food blender with stainless steel cutter.

2.0g of the homogenized sample was weighed into a digestion tube + 10 cm^3 of conc. HNO_3 , covered with watch glass and left overnight. In the next day, the sample was heated to 125°C until the liquor is clear. Followed by 10 cm^3 of HNO_3 + 4 cm^3 of HClO_4 + 4 cm^3 of H_2O_2 + 2 cm^3 of HCl , and the temperature was maintained at 135°C for 1 h until the liquor became colourless. Caution was taken to maintain excess HNO_3 and H_2O_2 until most of the organic materials are destroyed. The samples were evaporated slowly to almost dryness, cooled and dissolved in 5 cm^3 of 1 mol/L HNO_3 . The digested sample were filtered through Whatman number 1 filter paper and the filtrate was diluted to 25 cm^3 marks with 0.25 mol/dm^3 HNO_3 and showed for AAS analysis.

In this study, Statistical analysis was performed using Microsoft Excel 2010. Both descriptive and inferential statistical analyses were used to interpret the raw data in this study. Pearson correlation analysis was also carried out. The heavy metal concentrations in each matrix were determined by using a GBC Avanta Ver. 2.02 AAS.

3. RESULTS AND DISCUSSION

The results of the investigated heavy metals in sediments are summarized in Table 1. The mean values of heavy metals in fish tissues are presented in Tables 3-4 respectively.

The five heavy metals investigated in sediment and African catfish (*Clarias gariepinus*) tissue samples of the Kolo Creek in Niger Delta region, Nigeria, results are presented graphically in figures 2-4 as percent of heavy metal species.

3.1 Heavy metals Concentration in sediment samples

The mean concentration of extractable heavy metals from sediment of the Kolo Creek and comparison with sediment quality guidelines (SQGs) and US Environmental Protection Agency (USEPA) reference values are presented in Table 1. The mean concentrations of the metals (mg/kg) analyzed in the sediments decrease in sequence as: Fe (2241.1±1549.02) > Zn (35.19±22.15) > Cu (7.39) > Pb (6.00±4.47) > Cd (2.22±2.48) respectively.

Table 1. Heavy metals concentration (mg/kg) in sediments and comparison with reference values

Rivers	Parameters	Cd	Cu	Fe	Pb	Zn	Reference
Kolo creek	mean	2.22	7.39	2241.1	6.00	35.19	This study
	St. Dev.	2.48	4.75	1549.02	4.47	22.15	
Kolo creek	mean			3707.44	1.64		[14]
	St. Dev			1128.38	0.70		
Imo river	mean	0.30	2.28	2025.72	3.52	12.35	[19]
	St. Dev	0.1	1.20	304.4	1.7	9.0	
Reference values	USEPA	0.99	31.6		35.8	121	[26]
SQGs	Non polluted		<25		<40	<90	[22,24, 25]
	Moderately polluted		25-50		40 - 60	90 - 200	
	Heavily polluted		>50		>60	>90	
	TEL	0.68	18.70		30.20	124.00	[16, 4, 12]

The results obtained in this study were lower than the respective international reference values for [26]. The result obtained in this study for heavy metal concentrations agreed with those reported by [13], [18], [14] which are of the similar geographical region and study area with similar sources of contaminant input.

Assessment of sediment pollution based on SQGs and ecotoxicological sense of heavy metal contamination was employed. Sediments were classified as non-polluted, moderately polluted and heavily polluted based on SQGs [22],[24]. According to SQGs, the heavy metals studied in sediments of the Kolo Creek were under the category of non-polluted [25],[22]. The ecotoxicological sense of heavy metal contamination in sediments was employed using sediment quality guidelines developed for marine and estuarine ecosystem [16]., [4]., [12]., [24]. These effects are as follow: a) The effect range low (ERL) / effect range median (ERM) b) The threshold effect level (TEL) / probable effect level (PEL).The heavy metals studied in sediments of the Kolo Creek do not exceed TEL values which can lead to adverse impact on the sediments dwelling fauna (Table 1).

3.2 Statistical Evaluation of Data

The Pearson's correlation matrix (PCM) data are presented in Table 2. The PCM analysis provided a means of statistically ascertaining association/correlation of one parameter with another. PCM analysis reveals a positive correlation

between the metal ions; this could indicate a common source for all the metals, however, very few of the metals are significantly correlated with each other. This behavior could indicate non-point source.

Table 2. Correlation coefficients of heavy metals in the Kolo Creek

	Cd	Cu	Fe	Pb	Zn
Cd	1.00				
Cu	0.94	1.00			
Fe	0.98	0.94	1.00		
Pb	0.99	0.98	0.98	1.00	
Zn	0.79	0.89	0.70	0.83	1.00

3.3 Heavy metals concentration(mg/kg) African fish tissues

The result of heavy metals in fish samples are presented in Tables 3 and 4. Zinc levels in Kolo Creek African catfish (*clarias gariepinus*) samples ranged from 37.66 -17.69 with mean value of (26.86±8.24) mg/kg in gills and 27.19 -12.33 with mean value of (19.20 ± 6.11) mg/kg for muscles. The result obtained in this study for zinc concentrations agreed with those reported by [18], [20], [9] which are of the similar geographical region with similar sources of contaminant burden.

Table 3. Heavy metal concentration in *clarias gariepinus* tissues

metals	gills		muscle	
	range	Mean ±std	range	Mean ±std
cd	0.58 - 0.24	0.37±0.15	1.44 - 0.04	0.54±0.64
cu	6.23 - 1.42	3.21±0.15	1.91-0.36	1.25±1.76
fe	95.65 - 61.56	110.33±46.99	59.50 - 15.97	42.26±18.90
pb	3.79 - 0.46	1.60±1.55	2.33 - 0.36	1.16±0.84
zn	37.66 - 17.69	26.86±8.24	27.19 - 12.33	19.20±6.11

Table 4. Heavy metal concentration in *clarias gariepinus* tissues and comparison with reference values

RIVERS	FISH PARTS	parameters	Cd	Cu	Fe	Pb	Zn	REFERENCE
KOLO CREEK	GILL	mean	0.37	3.21	110.33	1.60	26.86	This study
		St. Dev.	0.15	0.15	46.99	1.55	8.24	
	MUSCLES	mean	1.25	42.26	1.16	19.20		
		St. Dev.	0.64	1.76	18.90	0.84	6.11	
IMO RIVER	GILLS	mean	0.47	0.13	14.64	1.24	4.08	[20]
		St. Dev	0.13	0.004	0.52	0.20	0.25	
	MUSCLES	mean	0.125	0.24	4.85	0.74	2.33	
		St. Dev	0.29	0.13	0.54	0.05	0.14	
FEPA			2.00	1.3	100	0.2	75	[11]
WHO			2.00	3.0	100	0.2	10-75	[27]

The data shows that, concentration (mg/kg) of cadmium in fish tissues ranged from 0.58 - 0.24 with mean value of 0.37 ± 0.15 in gills while it ranged from 1.44-0.04(0.54 ± 0.64) in muscles. A comparative analysis between cadmium levels in fish tissues from Kolo creek and [11] as reported in Table 3 shows that, values of cadmium in this study were low. The result obtained in this study for cadmium concentrations agreed with those reported by [18], [20], [9] which are of the same geographical region with similar sources of contaminant burden

The concentration of copper ranged between 6.23–1.42 mg/kg with an average of 3.21 ± 2.15 mg/kg in gills while it ranged from 1.91 – 0.36 mg/kg in muscles with an average of 1.25 ± 1.76 mg/kg. The levels were also lower in muscles but higher in gills when compared with levels in [27], [11]. The result obtained in this study for copper concentrations agreed with those reported by [18], [20], [9] which are of the same geographical region with similar sources of contaminant input

The concentration of iron ranged from 95.65 – 61.56 mg/kg with a mean (110.33 ± 46.99) mg/kg in gills while it ranged from 59.50–15.97 mg/kg in muscles with a mean of 42.26 ± 18.90 mg/kg. The levels were also low when compared with levels in [27], [11]. The result obtained in this study for iron concentrations agreed with those reported by [18], [20], [9], which are of the same geographical region with similar sources of contaminant burden

The values (mg/kg) for lead (range, mean \pm std) in gills and muscles were (3.79 - 0.46, 1.60 ± 1.55) and (2.33 - 0.36, 1.16 ± 0.84) respectively. The levels of lead were lower when compared to levels in [27], [11]. The result obtained in this study for lead concentrations agreed with those reported by [18], [20], [9] which are of the similar geographical region with similar sources of contaminant input.

The five heavy metals investigated in sediment and fish tissue samples of the Kolo Creek in Niger Delta region, Nigeria, results are presented in figures 2-4 as percent of heavy metal species.

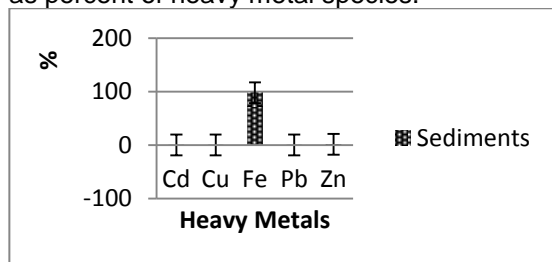


Fig.2. Percentage content of heavy metals in sediments

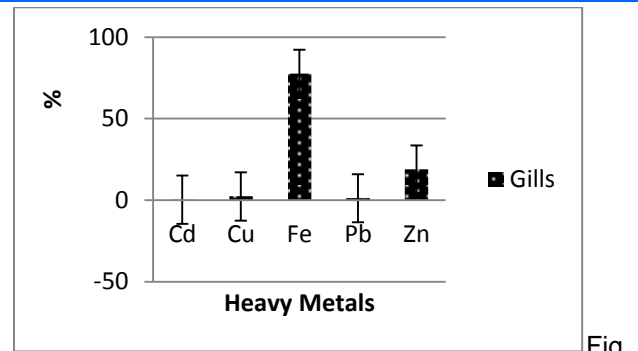


Fig. 3. Percentage content of heavy metals in gills

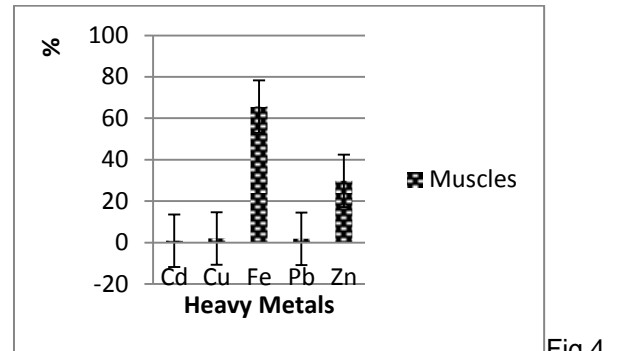


Fig.4. Percentage content of heavy metals muscles

4. CONCLUSION

The five heavy metals commonly examined based on their potential toxic effects include: Cd, Cu, Fe, Pb and Zn. The results showed that heavy metals investigated in the study area (Kolo Creek) were within the maximum allowed limits and do not pose any treat. In other words, the concentrations observed in the study area cannot cause severe to excessive pollution, capable of serious ecological and public health hazards. This implies that no significant heavy metal toxicity levels were observed and a low source of pollution arriving to the Kolo Creek. In conclusion, fish from the Kolo Creek are safe within the limits for human consumption, conservation and commercial purposes. Consequently, the regulatory authorities should be encouraged to institute environmentally friendly framework to maintain the immerse biodiversity and aesthetic value of the Kolo Creek

COMPETING INTERESTS

Authors have declared that no competing interests exist

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